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Tinsleyite, the aluminum analogue of leucophosphite, from the Tip Top pegmatite in South Dakota

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Abstract

Tinsleyite, $KAl_2(PO_4)_2(OH) \cdot 2H_2O$, is a new species from the Tip Top Mine, near Custer, South Dakota. It is monoclinic, space group Pn or $P2/n$, with a = 9.602(8), b = 9.532(6), c = 9.543(11)Å, β = 103.16(6)°, and Z = 4. The strongest powder diffraction lines are (d, I, hkl): 6.68,*10*,110,011; 5.91,*8*,101,$\bar{1}11$; 3.006,*7*,130,031,$\bar{1}13$; 2.616,*6*,032,$\bar{2}31$, $\bar{1}32$,320. Microprobe analysis yields K_2O 12.4, Fe_2O_3 5.2, Mn_2O_3 1.1, Al_2O_3 26.6, P_2O_5 42.2, H_2O (by difference) 12.5, sum = 100.0 weight percent.

Tinsleyite is dark magenta red, with pink streak, hardness (Mohs) approximately 5, and density 2.69 (meas.), 2.62 (calc.) g/cm^3. The luster is vitreous. Optically, tinsleyite is biaxial, positive, $2V = 86°$, with indices of refraction $\alpha = 1.591$, $\beta = 1.597$, $\gamma = 1.604$. It is strongly pleochroic with X = pale orange brown, Y = light purple, and Z = dark purplish red; absorption: $Z > Y > X$, $X = b$. Tinsleyite is associated with leucophosphite, rockbridgeite, tavorite, carbonate-apatite, and robertsite in highly altered triphylite pods in the pegmatite. Tinsleyite is chemically the Al-analogue of leucophosphite but apparently differs slightly in structure. Type material is deposited in the Smithsonian Institution under #159882. Tinsleyite is named in honor of Mr. Frank C. Tinsley of Rapid City, South Dakota.

Introduction

As part of a study of the mineralogy of the Tip Top pegmatite by one of the authors (TJC), several leucophosphite samples of unusual appearance were studied in detail. One of these, a magenta-colored material, first found in the late 1960's, was found to contain abundant Al. Our subsequent study has shown that these magenta-colored crystals are in part a new mineral, the Al-analogue of leucophosphite. Additional material was found in 1982 and some of this was found to be the new phase using optical methods.

We take pleasure in naming this mineral *tinsleyite* in honor of Mr. Frank C. Tinsley of Rapid City, South Dakota. Mr. Tinsley has been a long-term contributor to the preservation of rare and unusual specimens from the Tip Top pegmatite and many other localities in South Dakota. As a direct result of his efforts, much valuable research material has been saved from loss or destruction. The species and the name were approved by the IMA Commission on New Minerals and Mineral Names. Type material is preserved at the Smithsonian Institution and in the private collection of WLR.

Physical and optical properties

Tinsleyite occurs as thin, magenta-red layers on common Fe-rich leucophosphite with parting surfaces between the two species. Tinsleyite forms as the outermost zone of such composite crystals and approaches the composition given herein only in the 0.05 mm outer portions of the crystals. The streak is pink and the hardness is approximately 5 (Mohs). The luster is vitreous on crystal faces and fracture surfaces. The density of

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the outermost, most Al-rich, zone of tinsleyite is 2.69(5) g/cm^3, as determined using heavy liquid methods. This compares well with the calculated density of 2.62 g/cm^3. There is no visible fluorescence in ultraviolet radiation. Tinsleyite is brittle. The red color of tinsleyite (and some associated leucophosphite) is ascribed to trivalent manganese, as noted under "Chemistry."

Tinsleyite is biaxial, positive, $2V = 86°$ (measured and calculated), with indices of refraction $\alpha = 1.591$, $\beta = 1.597$, and $\gamma = 1.604$ (all ± 0.003). Tinsleyite is strongly pleochroic with X = pale orange-brown, Y = light purple, and Z = dark purplish red; absorption is $Z > Y > X$ and the orientation is $X \parallel b$. Dispersion is indiscernible due to the intense pleochroism. Color zoning is apparent in most crystals examined. Calculation of the Gladstone–Dale relationship using the constants of Mandarino (1981) yields $K_C = 0.216$ for the chemical composition and $K_P = 0.222$, indicating excellent compatibility of the chemical and physical data.

The above description applies to the holotype material, and it must be emphasized that not all the magenta-colored material examined was tinsleyite. Some of the material was essentially pure leucophosphite with only traces of Al, and the dark red color of tinsleyite is, therefore, not a useful diagnostic property. Optical examination, emphasizing indices of refraction, and X-ray powder diffraction data are the most reliable means for the differentiation of these two closely-related species in those cases where chemical analysis is not possible.

Chemistry

Tinsleyite was chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. The standards used were microcline (K), montgomeryite (P,Al), manganite (Mn), and maricite (Fe). The data were corrected using standard Bence-Albee factors. A wavelength-dispersive microprobe scan indicated the absence of other elements with atomic number greater than 8. The resultant analysis is: K_2O 12.4, Fe_2O_3 5.2, Mn_2O_3 1.1, Al_2O_3 26.6, P_2O_5 42.2, H_2O (by difference) = 12.5, sum = 100.0 percent. Mn is assumed to be Mn^{3+} because of the intimate association with robertsite and the dark red color, which is consistent with the absorption of Mn^{3+} in the visible range. Water was calculated by difference because of extreme paucity of material; the validity of this assumption is supported by the known crystal structural formula of leucophosphite (Moore, 1972). Calculation of the chemical formula of tinsleyite, based on P = 2, yields: $K_{0.89}(Al_{1.75}Fe^{3+}_{0.22}Mn^{3+}_{0.05})_{\Sigma 2.02}(PO_4)_2(OH)_{0.95} \cdot 1.86H_2O$ or, ideally, $KAl_2(PO_4)_2(OH) \cdot 2H_2O$ with Z = 4.

Crystallography

Tinsleyite occurs as monoclinic crystals of tabular prismatic habit essentially identical to that of leucophosphite (Lindberg, 1957). The forms present, indexed on the basis of the primitive cell described below, are $\{\bar{1}01\}$, $\{\bar{1}11\}$, $\{011\}$, and $\{110\}$. Tinsleyite crystals are tabular on $\{\bar{1}01\}$. An SEM micrograph of a representative crystal is shown in Figure 1.

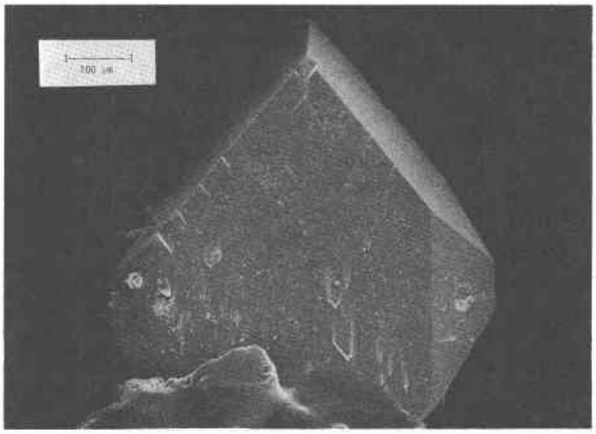

Fig. 1. Tinsleyite crystal from Tip Top pegmatite. The large crystal face is $(\bar{1}01)$.

The crystal fragment chosen for X-ray study was a composite (as were *all* fragments), consisting of a colorless leucophosphite core enveloped by magenta-colored tinsleyite. Precession photographs taken with Mo$K\alpha$ and Cu$K\alpha$ radiations showed two, nearly coincident, primitive monoclinic lattices. One had cell parameters $a = 9.77$, $b = 9.65$, $c = 9.75$Å, and $\beta = 103.4°$, which agree within 0.01Å with those reported by Moore (1972) for leucophosphite from the Tip Top mine. There is also a close correspondence to the cells of the Brazilian material (Lindberg, 1957) and synthetic leucophosphite (Smith and Brown, 1959). The second lattice had cell parameters 0.1 to 0.2Å less than those of the first and is ascribed to tinsleyite. Their refined values, which were derived from the powder diffraction data (Table 1) using least-squares and an NBS silicon internal standard ($a = 5.43088$Å), are $a = 9.602(8)$, $b = 9.532(6)$, $c = 9.543(11)$Å, and $\beta = 103.16(6)°$. Tinsleyite reflections were slightly out-of-focus on the precession photographs. This indicates a slight difference in orientation of the two species in the composite crystals, which may be regarded as epitaxial overgrowths of tinsleyite on leucophosphite.

The space group of tinsleyite is *Pn* or *P2/n*, which differs from that of leucophosphite ($P2_1/n$) in its lack of screw axes. This is proven by the presence of a weak 010 reflection on the Cu$K\alpha$ precession photographs, the other odd orders along b^* being absent. As the powder data (Table 1) also contain a weak but distinct line at 9.59Å, which can only be indexed as 010 ($d_{calc.} = 9.53$Å), the precession spot cannot be dismissed as an extraneous reflection due to multiple diffraction or anode contamination. None of the published powder data for leucophosphite contains this line and an examination of all leucophosphite powder photographs in the Smithsonian

Table 1. X-ray powder diffraction data for tinsleyite

I	d_{obs}	d_{calc}	hkl
1	9.59	9.53	010
1	7.48	7.50	$\bar{1}01$
10	6.68	6.67	110
		6.65	011
8	5.91	5.95	101
		5.89	$\bar{1}11$
4	4.66	4.68	200
		4.65	002
4	4.235	4.241	021
5	4.157	4.157	$\bar{2}11$
1	4.009	4.022	$\bar{1}21$
5	3.723	3.719	121
1	3.486	3.489	$\bar{2}12$
4	3.319	3.327	022
		3.317	$\bar{2}21$
		3.309	$\bar{1}22$
<<1	3.164	3.163	$\bar{1}03$
7	3.006	3.008	130
		3.006	031
		3.002	$\bar{1}13$
4	2.936	2.946	013
		2.926	$\bar{1}31$
5	2.836	2.839	212
5	2.773	2.778	$\bar{2}13$
		2.771	301
6b	2.616	2.623	032
		2.618	$\bar{2}31$
		2.614	132
		2.608	320
<<1	2.525	2.523	322
<1	2.447	2.448	231
		2.445	132
<<1	2.382	2.383	040
4	2.321	2.327	$\bar{4}11$
		2.323	004
<<1	2.234	2.235	$\bar{2}14$
<<1	2.218	2.218	033
<1	2.131	2.133	$\bar{1}24$
1	2.101	2.101	411
<<1	2.059	2.057	$\bar{3}14$
<1	1.963	1.965	$\bar{3}33$
<1	1.925	1.927	$\bar{3}24$
		1.920	402
<<1	1.894	1.893	340
<<1	1.780		
<<1	1.752		
<1	1.726		
<<1	1.666		
<1b	1.630		
<<1	1.589		
<<1	1.558		
<<1	1.532		
<1	1.501		
1	1.468		
<<1	1.416		
<<1	1.304		

114.6 mm Gandolfi camera, CuKα radiation, visually estimated intensities, polycrystalline specimen, b = broadened line. Reflections indexed with the aid of the precession photographs.

Institution file produced the same negative result. Tinsleyite also possesses a *B*-centered pseudo-orthorhombic cell like that of leucophosphite. The $B2_1/n$ symmetry reported for the latter cell by Lindberg (1957) is presumably a misprint for $B2_1/c$.

In his solution of the crystal structure of leucophosphite, Moore (1972) found that it contains tetrameric clusters of FeO_6 octahedra related by the operations of the 2_1 axes. If tinsleyite is essentially isostructural with its iron analogue, the low intensity of 010 and the absence of higher orders of $0k0$, $k = 2n + 1$ reflections suggests that the tetramers are still related by pseudo-screw symmetry. In view of this and the fact that a twofold rotation is inconsistent with the leucophosphite structure, the probable space group of tinsleyite must be Pn rather than $P2/n$. In summary, while tinsleyite is, in the exact sense, the chemical analogue of leucophosphite, the structural analogy is only approximate.

Occurrence

Tinsleyite occurs in the Tip Top pegmatite, located just southwest of the center of Section 8, T4S, R4E, approximately 5.5 miles southeast of Custer, South Dakota. Tinsleyite is moderately abundant and is found in highly-altered triphylite pods within the intermediate zone of the pegmatite. This zone consists of large perthite crystals with quartz, muscovite, fluorapatite, albite, beryl, minor elbaite, and columbite-tantalite. In most cases, the triphylite has been totally altered to secondary phosphates.

Rockbridgeite-frondelite and tavorite are among the earliest secondary phosphates formed with rockbridgeite being dominant. Green, prismatic leucophosphite crystals about 5 mm in length formed subsequent to rockbridgeite-frondelite and tavorite. Tinsleyite formed after leucophosphite on which it commonly occurs as morphologically continuous overgrowths. Tinsleyite is found as deep reddish-purple (magenta) colored crystals. Black, spherical aggregates of robertsite, together with yellow-orange, prismatic crystals of a jahnsite-group mineral, formed subsequent to leucophosphite and tinsleyite. Other minerals younger than tinsleyite include white, radial aggregates of carbonate-apatite and orange, prismatic crystals of laueite.

Acknowledgments

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